

Stochastic aggregation: rate equations approach

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Abstract. We investigate a class of *stochastic*-aggregation processes involving two types of clusters: active and passive. The mass distribution is obtained analytically for several aggregation rates. When the aggregation rate is constant, we find that the mass distribution of passive clusters decays algebraically. Furthermore, the entire range of acceptable decay exponents is possible. For aggregation rates proportional to the cluster masses, we find that gelation is suppressed. In this case, the tail of the mass distribution decays exponentially for large masses, and as a power law over an intermediate size range.

1. Introduction

Aggregation, coagulation or agglomeration are kinetic phenomena in which clusters bond irreversibly to form clusters of indefinitely growing mass. A detailed model of the merging of two clusters into a single cluster should incorporate the mass, position, velocity (or diffusion rate) and even geometrical characteristics of each cluster, together with the precise merging mechanism. Such a detailed description is well beyond theoretical analysis. The most natural approach *assumes* that the merging of two clusters of masses x and y into a cluster of mass $x + y$ occurs with a rate kernel $K(x, y)$. The cluster densities then evolve according to the Smoluchowski coagulation equations [1]. This theoretical framework [1–5] has been found numerous applications in physical chemistry [6], as well as in astronomy [7] and mathematics [8].

Characterizing a cluster by a single parameter, its mass, may indeed be a drastic oversimplification. For instance, two clusters with a similar mass can be substantially different. Additionally, the character of a cluster may be altered every time it undergoes aggregation, and, for example, it may become less likely to participate in further aggregation events. In this paper, we investigate situations where active clusters may become passive after merging events. A concrete example where active and passive clusters coexist are multi-phase coarsening processes in one dimension. Indeed, upon merging, domain walls may remain active or become passive depending on the phase of their neighbouring domains [9–11]. Another example is the polymerizations of linear polymers. Here, if the end monomers are chemically active or inert, newly produced polymers may become passive. Scaling properties and numerical studies of several stochastic-aggregation problems will be presented in a subsequent paper [12].

Specifically, we consider a class of models where newly formed clusters remain active with a fixed probability p ; otherwise, they become passive in the sense that they never aggregate again. As the fate of newly formed clusters is determined stochastically, we term this process

stochastic aggregation. Given a fixed probability for active clusters to become passive, all clusters eventually become passive, and the system freezes. Our goal is to determine the time-dependent distributions of active and passive clusters, as well as the final mass distribution of passive clusters.

Within the standard framework [1, 2], it has long been recognized that the Smoluchowski master equations are tractable for three particular kernels: $K(x, y) = 1$, $x + y$ and xy [3]. Exact results have also been found for linear combinations of these solvable kernels [13, 14], and for one nonlinear interpolation between the constant and sum kernels [15]. As will be shown, stochastic aggregation is solvable for the three classical kernels.

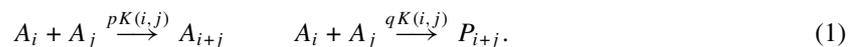
For instance, in the simplest case of mass-independent aggregation rates, we find that P_k , the final mass distribution of passive clusters, is scale free, i.e. $P_k \sim k^{-\gamma}$. Since $\gamma = 2/p$, the entire range of decay exponents $2 < \gamma < \infty$ is realized by tuning $0 < p < 1$. Similar behaviour emerges in a dual fragmentation process where newly formed fragments may become passive [16]. In contrast, both the sum and the product kernels are characterized by final mass distributions which are suppressed exponentially for large masses. Nevertheless, over an intermediate size range, an algebraic decay with a fixed decay exponent may occur. The time-dependent behaviour is governed by an algebraically growing size scale, and it can be cast as either a scaling or a scaling-like form. In general, the growth law for this scale is not universal as it depends on the parameter p .

The rest of this paper is organized as follows. In section 2 we define the model and outline the general framework. Exact solutions of the master equations for the cases of constant, product and sum kernels are presented in sections 3, 4, and 5, respectively. The results are summarized and discussed in section 6.

2. The model

Consider the initial conditions where all clusters are active and have the same mass, which can be set to unity without loss of generality. Then, active monomers aggregate to form dimers, and so on. After an aggregation event, the newborn cluster remains active with probability p , or becomes passive with probability $q = 1 - p$. In the latter case, the cluster does not undergo further aggregation.

Let $K(i, j)$ be the rate at which clusters of mass i and clusters of mass j aggregate, and let A_k (P_k) denote active (passive) clusters of mass k . The stochastic-aggregation process can be symbolically written as



We use the notation $A_k(t)$ and $P_k(t)$ to denote the density distributions of active and passive clusters at time t . The master equations describing the time evolution of the system read

$$\begin{aligned} \frac{dA_k}{dt} &= \frac{1}{2}p \sum_{i+j=k} K(i, j)A_iA_j - A_k \sum_{j \geq 1} K(k, j)A_j \\ \frac{dP_k}{dt} &= \frac{1}{2}q \sum_{i+j=k} K(i, j)A_iA_j. \end{aligned} \quad (2)$$

The convolution terms are proportional to p and q , respectively, reflecting the probabilities of remaining active and becoming passive after each aggregation event. The master equations are subject to monodisperse initial conditions

$$A_k(0) = \delta_{k,1} \quad P_k(0) = 0. \quad (3)$$

One may verify that the overall mass is conserved, i.e. $\sum_{k \geq 1} k[A_k(t) + P_k(t)] = 1$.

We are interested in the temporal behaviour of the mass distributions of both active and passive clusters, and in the final distribution of passive clusters. An important feature of the model is that the number densities of active and passive clusters are ultimately related throughout the evolution. Indeed, in each aggregation event the total number of active clusters is reduced by 1 with probability p , or by 2 with probability q ; hence on average it reduces by $1 + q$. Simultaneously, each aggregation event increases the total number of passive clusters by q on average. Thus, the following properly weighted combination of the number densities $A(t) = \sum_{k \geq 1} A_k(t)$ and $P(t) = \sum_{k \geq 1} P_k(t)$ is conserved:

$$qA(t) + (1 + q)P(t) = \text{constant}. \tag{4}$$

This second conservation law also follows from the rate equations. However, it holds generally for stochastic-aggregation processes, even when the master equations (2) do not apply.

Assuming that initially there were no passive clusters, $P(0) = 0$, and setting the initial cluster density to one, $A(0) = 1$, we see that equation (4) gives a neat expression for the final number density of passive clusters

$$P(\infty) = \frac{q}{1 + q}. \tag{5}$$

Additionally, mass conservation implies $\sum_k kP_k(\infty) = 1$, and therefore the average mass of a passive cluster is $(1 + q)/q$. A q^{-1} divergence occurs in the $q \rightarrow 0$ limit, corresponding to traditional aggregation. Remarkably, the final density (or equivalently, the average mass) is independent of the details of the model such as the aggregation kernel, the transport mechanism of the clusters, or the dimensionality of the system.

We proceed to solve the master equations for three different kernels: constant $K(i, j) = 2$, product $K(i, j) = ij$ and sum $K(i, j) = i + j$. Although we restrict our attention to monodisperse initial conditions, our techniques apply to arbitrary initial conditions. Furthermore, the nature of the solutions extends to compact initial distributions.

3. The constant kernel

The constant kernel is the one most widely used. It has been applied to diffusion limited coalescence, for example. In traditional aggregation with $K(i, j) = \text{constant}$, the typical mass grows linearly with time, and the mass distribution is exponential. We shall see that the latter assertion also applies to stochastic aggregation.

We conveniently set $K(i, j) = 2$, and the master equations read

$$\begin{aligned} \frac{dA_k}{dt} &= p \sum_{i+j=k} A_i A_j - 2A A_k \\ \frac{dP_k}{dt} &= q \sum_{i+j=k} A_i A_j. \end{aligned} \tag{6}$$

The number densities of active and passive clusters can be obtained directly. The reaction proceeds through two channels: $A + A \rightarrow A$ with rate p and $A + A \rightarrow P$ with rate q , and, therefore, the number densities obey

$$\frac{dA}{dt} = -(1 + q)A^2 \quad \frac{dP}{dt} = qA^2. \tag{7}$$

Solving these equations subject to the initial conditions $A(0) = 1$ and $P(0) = 0$ gives

$$A(t) = \frac{1}{1 + (1 + q)t} \quad P(t) = \frac{qt}{1 + (1 + q)t}. \tag{8}$$

Indeed, the relation (4) between A and P holds, and the final density $P(\infty) = q/(1+q)$ is recovered. Additionally, the density of active clusters decays algebraically with a universal exponent: $A \sim t^{-1}$.

One can also study the mass density of active clusters $M(t) = \sum_{k \geq 1} k A_k(t)$. This quantity has a nice probabilistic interpretation: it equals the survival probability of an active monomer initially present in the system. In other words, it is the probability that such monomer belongs to an active cluster at time t . From equation (6) we find that the mass density evolves according to $\frac{d}{dt} M = -2qAM$. Using $A(t)$ from equation (8) and the initial condition $M(0) = 1$, we integrate the rate equation to find

$$M(t) = [1 + (1+q)t]^{-2q/(1+q)}. \quad (9)$$

Hence, the decay of the total mass density and the growth of the average cluster size exhibit non-universal behaviour as they depend on the parameter q : $M \sim t^{-2q/(1+q)}$ and $\langle k \rangle = M/A \sim t^{p/(1+q)}$, respectively. Note also that the linear average mass growth, $\langle k \rangle \sim t$, is recovered for the traditional aggregation process $p = 1$. Similarly, the monomer density $A_1(t) = [1 + (1+q)t]^{-2/(1+q)}$, obtained from $\frac{d}{dt} A_1 = -2AA_1$, exhibits an algebraic decay with a q -dependent exponent. This quantity is the probability that a monomer avoids aggregation events up to time t .

We solve for the mass distribution of active clusters first. To this end, we transform the distribution A_k and introduce a modified time variable τ as follows:

$$\begin{aligned} \mathcal{A}_k &= A_k \exp \left[2 \int_0^t dt' A(t') \right] \\ \tau &= p \int_0^t dt_1 \exp \left[-2 \int_0^{t_1} dt_2 A(t_2) \right]. \end{aligned} \quad (10)$$

The modified time variable can be written explicitly, $\tau = 1 - [1 + (1+q)t]^{-p/(1+q)}$. In terms of this time variable one has $A = (1 - \tau)^{(1+q)/p}$ and $\mathcal{A}_k = A_k(1 - \tau)^{-2/p}$. The above transformations reduce equation (6) to

$$\frac{d\mathcal{A}_k}{d\tau} = \sum_{i+j=k} \mathcal{A}_i \mathcal{A}_j. \quad (11)$$

These equations can be solved by the generating-functions technique. Indeed, $\mathcal{A}(z, \tau) = \sum_{k \geq 1} e^{kz} \mathcal{A}_k(\tau)$ obeys

$$\frac{\partial \mathcal{A}(z, \tau)}{\partial \tau} = \mathcal{A}^2(z, \tau). \quad (12)$$

The solution is given by $\mathcal{A}(z, \tau) = A_0(z)[1 - \tau A_0(z)]^{-1}$, with $A_0(z) \equiv A(z, 0) = \mathcal{A}(z, 0)$ the initial generating function. For the monodisperse initial conditions (3), $\mathcal{A}_0(z) = e^z$, and we find $\mathcal{A}_k = \tau^{k-1}$. Thus, the original mass distribution reads

$$A_k(\tau) = (1 - \tau)^{2/p} \tau^{k-1} \quad (13)$$

i.e. it remains exponential throughout the evolution. Although we present this solution as a function of τ , it is an explicit solution as $\tau(t)$ is known.

The passive-cluster distribution can be obtained by integrating the corresponding master equation. Again, it is more convenient to use the modified time variable as equation (6) simplifies to $\frac{d}{d\tau} P_k = \frac{q}{p} (k-1)(1 - \tau)^{2/p} \tau^{k-2}$. Integrating over the modified time gives

$$P_k(\tau) = \frac{q}{p} (k-1) \int_0^\tau dx (1-x)^{2/p} x^{k-2}. \quad (14)$$

The final distribution is obtained by setting $\tau = 1$. It can be expressed in terms of the Euler Gamma function

$$P_k(\infty) = \frac{q}{p} \frac{\Gamma(1 + 2/p) \Gamma(k)}{\Gamma(k + 2/p)}. \tag{15}$$

The large-mass tail of the distribution is therefore suppressed algebraically according to

$$P_k(\infty) \simeq qp^{-1} \Gamma(1 + 2/p) k^{-2/p}. \tag{16}$$

Interestingly, given the algebraic decay $P_k \sim k^{-\gamma}$ as $k \rightarrow \infty$, mass conservation restricts the exponent range to $\gamma > 2$. In our case $\gamma = 2/p$, and since $0 < p < 1$, the entire range of acceptable exponents emerges by tuning the only control parameter p . This behaviour is reminiscent of a related stochastic-fragmentation process where newly formed fragments may turn stable [16].

Despite their different limiting behaviours, both mass distributions obey the same scaling form. This reflects the nature of the process: the distributions are coupled, and the ‘activity’ in the system involves masses of the order of the characteristic mass. To obtain the scaling forms, we consider the limit $k \rightarrow \infty$ and $t \rightarrow \infty$, with the scaling variable $\xi = k(1 - \tau)$ kept finite. In this limit, equations (13) and (14) acquire the following scaling forms:

$$A_k(t) \sim t^{-2/(1+q)} F(\xi) \quad P_k(t) \sim t^{-2/(1+q)} G(\xi) \tag{17}$$

with the scaling functions

$$F(\xi) = \exp(-\xi) \quad G(\xi) = \xi^{-2/p} \Gamma(1 + 2/p, \xi). \tag{18}$$

Here, $\Gamma(a, \xi) = \int_{\xi}^{\infty} dx x^{a-1} e^{-x}$ is the incomplete Gamma function. The scaling variable $\xi = k/k^*$ contains the characteristic mass $k^* = (1 - \tau)^{-1} = \langle k \rangle \sim t^{p/(1+q)}$. At time t , the mass of passive clusters being produced is on the order k^* . Masses larger than this scale are exponentially rare as $G(\xi) \propto F(\xi) = e^{-\xi}$. On the other hand, masses smaller than this scale have already turned passive. This is manifested by the small argument divergence $G(\xi) \sim \xi^{-2/p}$, which leads to the time-independent algebraic distribution (16).

In fact, the scaling functions are unique. When the initial mass is finite, the scaling exponents and, consequently, the scaling form (17) are dictated by the rate equations for the number and mass densities. Substituting this scaling form into the rate equations (6) yields an integro-differential equation for the scaling function $\int_0^{\xi} d\eta F(\eta) F(\xi - \eta) + \xi F'(\xi) = 0$. This equation can be solved via the Laplace transform, and provided that the first two moments of F are finite, the solution is a simple exponential. A similar analysis can also be carried for the second scaling function. We conclude that the above scaling behaviour holds, in general, for compact initial distributions.

4. The product kernel

The aggregation process with a reaction rate proportional to the mass of both reactants, $K(i, j) = ij$, has been applied to the polymerizations of branched polymers [3], and to random graphs [17]. In this case, the system exhibits a phase transition. Specifically, the mass condenses into an infinite cluster. In the following, we show that gelation does not occur when there is a finite probability for clusters to turn passive.

In this case, the master equations (2) read

$$\begin{aligned} \frac{dA_k}{dt} &= \frac{1}{2} p \sum_{i+j=k} ij A_i A_j - k A_k M \\ \frac{dP_k}{dt} &= \frac{1}{2} q \sum_{i+j=k} ij A_i A_j. \end{aligned} \tag{19}$$

Here too $M(t) = \sum_{k \geq 1} k A_k(t)$ is the mass density of active clusters. Let us start with analysis of the active-cluster distribution. To facilitate the solution, we again employ the generating-functions technique. Specifically, the generating function of the sequence $k A_k$, $\mathcal{A}(z, t) = \sum_{k \geq 1} k A_k(t) e^{kz}$, evolves according to

$$\frac{\partial \mathcal{A}}{\partial t} = (p\mathcal{A} - M) \frac{\partial \mathcal{A}}{\partial z}. \quad (20)$$

It is useful to rewrite partial derivatives as Jacobians:

$$\frac{\partial \mathcal{A}}{\partial t} = \frac{\partial(\mathcal{A}, z)}{\partial(t, z)} \quad \text{and} \quad \frac{\partial \mathcal{A}}{\partial z} = \frac{\partial(\mathcal{A}, t)}{\partial(z, t)}.$$

Substituting these Jacobians into equation (20), and using the cyclic-relation

$$\frac{\partial z}{\partial t} = \frac{\partial(z, \mathcal{A})}{\partial(t, \mathcal{A})}$$

we arrive at

$$\frac{\partial z}{\partial t} = M - p\mathcal{A}. \quad (21)$$

This equation suggests that one should solve for $z(\mathcal{A}, t)$. Integrating equation (21) gives a solution up to an arbitrary constant $F(\mathcal{A})$: $z(\mathcal{A}, t) = \int_0^t dt' M(t') - pt\mathcal{A} + F(\mathcal{A})$. The initial conditions (3) read $\mathcal{A}_0(z) = e^z$ or alternatively, $F(\mathcal{A}) = \ln \mathcal{A}$, thereby leading to

$$z(\mathcal{A}, t) = \int_0^t dt' M(t') - pt\mathcal{A} + \ln \mathcal{A}. \quad (22)$$

Therefore, the problem is now reduced to an evaluation of the mass density of active clusters $M(t)$. Substituting $\mathcal{A}(z = 0, t) = M(t)$ into equation (22) gives

$$\int_0^t dt' M(t') - ptM(t) + \ln M(t) = 0. \quad (23)$$

Differentiating this equation leads to $(ptM - 1) \frac{dM}{dt} = qM^2$. Rather than solve for $M(t)$, one can obtain an explicit solution for $t(M)$. Indeed, the first-order differential equation $qM^2 \frac{dt}{dM} - ptM = -1$ can be easily solved by a number of techniques, e.g., by a variation of the parameters, to give

$$t = M^{-1} - M^{p/q}. \quad (24)$$

As a check of self-consistency, we confirm that this expression agrees with the first-order Taylor series for the mass $M(t) \cong 1 - qt$, implied by master equation (19). Equation (24), in principle, gives the mass density $M(t)$. To determine the number density $A(t)$, we sum up equations (19) and find $\frac{dA}{dt} A = -\frac{1}{2}(1+q)M^2$. Since we have an explicit expression for $t(M)$ rather than $M(t)$, we treat A as a function of M as well. The density obeys

$$\frac{dA}{dM} = \frac{1}{2}(1+q) \left[1 + \frac{p}{q} M^{1/q} \right]$$

which can be integrated to yield

$$A(M) = \frac{1}{2} M \left[1 + q + pM^{1/q} \right]. \quad (25)$$

Equations (24) and (25) show that both the number and mass densities of active clusters decay similarly in the long-time limit,

$$A(t) \simeq \frac{1}{2}(1+q)t^{-1} \quad M(t) \simeq t^{-1}. \quad (26)$$

The decay exponent is universal and identical to that of the constant-kernel model. In that case, however, only the number density decayed as t^{-1} . Equation (26) also offers insight into the nature of the process as the average mass approaches a constant $\langle k \rangle = M/A \rightarrow 2/(1+q)$. One can verify that this quantity approaches unity in the limit $q \rightarrow 1$ when the active mass distribution contains only monomers.

To complete the solution, we need to determine A_k . Note that equation (22) can be rewritten as $\mathcal{A} e^{-ptA} = \exp \left[z - \int_0^t dt' M(t') \right]$. The Lagrange inversion formula is quite useful here [18]. It states that the solution for the equation $ve^{-v} = u$ can be expressed in terms of the series $v = \sum_{n \geq 1} \frac{n^{n-1}}{n!} u^n$. Applying it to the above equation yields

$$A_k(t) = \frac{(kpt)^{k-1}}{k \cdot k!} \exp \left[-k \int_0^t dt' M(t') \right]. \tag{27}$$

We again express A_k as a function of M rather than t . The integral can be read from equation (23), while the time $t(M)$ can be read from (24). Substituting the corresponding expressions yields the active-cluster mass distribution in terms of the variable $v = M^{1/q}$

$$A_k(v) = v^q \frac{[kp(1-v)]^{k-1}}{k \cdot k!} e^{-kp(1-v)}. \tag{28}$$

In the large-mass limit, the leading behaviour of this mass distribution is given by

$$A_k(v) \simeq \frac{v^q}{\sqrt{2\pi p^2(1-v)^2}} k^{-5/2} e^{-\Lambda(v,q)k} \tag{29}$$

with the decay constant $\Lambda(v, q) = qv - [q + \ln(1 - q)] - [v + \ln(1 - v)]$. This constant must be positive and this is confirmed by the expansion $\Lambda(v, q) = qv + \sum_{n \geq 2} n^{-1}(q^n + v^n)$. Therefore, the mass distribution decays exponentially with mass. This, in particular, implies that no gelation occurs. However, over an intermediate range $k \ll \Lambda^{-1}(v, q)$, the mass distribution decays algebraically, $A_k \sim t^{-1}k^{-5/2}$. Furthermore, the monomer density equals $A_1 = M e^{-p+pM^{1/q}}$, and in the long-time limit $A_1 \simeq e^{-p}t^{-1}$.

The asymptotic behaviour is of special interest. In the limit $k \rightarrow \infty$ and $t \rightarrow \infty$ with the scaling variable $\xi = kv$ kept finite, the mass distribution of active clusters can be recast into a ‘scaling-like’ form,

$$A_k(t) \sim e^{-\Lambda(q)k} k^{-5/2} t^{-1} F(\xi) \tag{30}$$

with $\Lambda(q) = -q - \ln(1 - q)$. The scaling function is simply exponential: $F(\xi) = e^{-\xi}$. The above differs from an ordinary scaling form in that it cannot be reduced from two variables (k, t) to one rescaled variable. Furthermore, the exponential factor $e^{-\Lambda k}$ indicates that the mass distribution is appreciable over a fixed-mass range of the order $1/\Lambda(q)$. This range is significant only in the (traditional aggregation) limit $q \rightarrow 0$. In this case, a universal algebraic decay $A_k \sim t^{-1}k^{-5/2}$ is realized in the intermediate mass range $k \ll q^{-2}$. Despite this, it is interesting that the distribution is characterized by a scaling-like factor, with a scaling variable $\xi = k/k^*$. Note that the characteristic mass grows with time, $k^* \sim q^{-1}t^{1/q}$, although the average mass $\langle k \rangle$ remains finite.

Turning to passive clusters, we first note that their number density can be obtained using $A(M)$ of equation (25) and conservation law (4)

$$P(M) = \frac{q}{1+q} - \frac{qM}{2} \left[1 + \frac{p}{1+q} M^{1/q} \right]. \tag{31}$$

Alternatively, this density can be obtained by integrating $\frac{d}{dt}P = \frac{1}{2}qM^2$. While the final number density (5) is universal, the mass distribution of passive clusters is model dependent.

In the previous case of the constant kernel, we evaluated the convolution term in the master equation explicitly. In the present case, it is more convenient to circumvent this sum by noting that it appears in both evolution equations. The evolution equation for $P_k(t)$ can therefore be simplified to $\frac{d}{dt}P_k(t) = \frac{q}{p}[\frac{d}{dt}A_k + kA_kM]$ for $k \geq 2$. Again, we present the mass distribution in terms of $v = M^{1/q}$:

$$P_k(v) = \frac{q}{p} \left[A_k(v) + \int_v^1 dx \frac{q + px}{x^p} \frac{[kp(1-x)]^{k-1}}{k!} e^{-kp(1-x)} \right]. \quad (32)$$

The final distribution $P_k(\infty)$ can be written explicitly using $\int_0^1 dx x^{l-1}(1-x)^{k-1}e^{\beta x} = B(l, k) {}_1F_1(l, l+k, \beta)$, with $B(l, k) = \Gamma(l)\Gamma(k)/\Gamma(l+k)$ the Euler Beta function and ${}_1F_1(a, b, x)$ the confluent hypergeometric function [19]. Additionally, it is possible to evaluate the large-mass asymptotic behaviour, as the above integral is dominated by a region of the order $\mathcal{O}(k^{-1})$ near the upper limit. Introducing the variable $y = xk$, keeping only the leading terms and performing the integration yields

$$P_k(\infty) \simeq \frac{q^{1+p} \Gamma(q)}{\sqrt{2\pi p^2}} k^{-q-3/2} e^{-k\Lambda(q)} \quad (33)$$

with $\Lambda(q)$ as in equation (30). Regardless of q , the tail of the distribution decays exponentially. However, in the limit $q \rightarrow 0$, a universal algebraic decay $P_k(\infty) \sim k^{-3/2}$ occurs in the intermediate regime $k \ll q^{-2}$. The average mass divergence q^{-1} agrees with equation (5). Hence, the behaviour is fundamentally different from that found for mass-independent rates as the distribution of masses of passive clusters is characterized by a finite scale.

The passive mass distribution (32) can be recast into a ‘scaling-like’ form. Using the same scaling variable $\xi = kv$, one finds

$$P_k(t) \simeq P_k(\infty) \frac{\Gamma(q, \xi)}{\Gamma(q)}. \quad (34)$$

This form involves the incomplete Gamma function, as was the case for function $G(\xi)$ in the case of the constant kernel (see equation (18)). Despite their very different natures, the mass distributions of passive clusters in both constant- and product-kernel models have a surprising similarity. Indeed, the former distribution (14) can be written in the form (34) with q replaced by $1 + 2/p$.

5. The sum kernel

The aggregation process with a linear reaction rate, $K(i, j) = i + j$, has been studied because of its mathematical simplicity as well as its relevance to polymer formation [20] and to shear-flow coagulation [3]. The sum-kernel solution is described concisely since it involves techniques similar to those used above. The mass distributions evolve according to

$$\begin{aligned} \frac{dA_k}{dt} &= \frac{1}{2}pk \sum_{i+j=k} A_i A_j - A_k(kA + M) \\ \frac{dP_k}{dt} &= \frac{1}{2}qk \sum_{i+j=k} A_i A_j. \end{aligned} \quad (35)$$

We introduce the modified densities \mathcal{A}_k and the modified time variable τ as follows:

$$\begin{aligned} \mathcal{A}_k &= A_k \exp \left[k \int_0^t dt' A(t') + \int_0^t dt' M(t') \right] \\ \tau &= p \int_0^t dt_1 \exp \left[- \int_0^{t_1} dt_2 M(t_2) \right]. \end{aligned} \quad (36)$$

These transformations reduce equation (35) into

$$\frac{d\mathcal{A}_k}{d\tau} = \frac{1}{2} k \sum_{i+j=k} \mathcal{A}_i \mathcal{A}_j. \tag{37}$$

The generating function $\mathcal{A}(z, \tau) = \sum_{k \geq 1} \mathcal{A}_k(\tau) e^{kz}$ evolves according to $\frac{\partial \mathcal{A}}{\partial \tau} = \mathcal{A} \frac{\partial \mathcal{A}}{\partial z}$, which in turn can be rewritten as $\frac{\partial z}{\partial \tau} = -\mathcal{A}$. Thus, for the monodisperse initial conditions, we obtain

$$z = \ln \mathcal{A} - \tau \mathcal{A}. \tag{38}$$

Again, the crucial part of the solution is the evaluation of the number and mass densities $A(t)$ and $M(t)$. These are related via the rate equation $\frac{d}{dt} A = -(1+q)AM$, as follows from equations (35). Integrating over time we obtain

$$A^{1/(1+q)} = \exp \left[- \int_0^t dt' M(t') \right]. \tag{39}$$

Inserting this equality into the definition of the generating function and using equation (36), yields $\mathcal{A} = A^{q/(1+q)}$ for $z = - \int_0^t dt' A(t')$. Substituting this equality into equation (38) gives

$$\ln A^{q/(1+q)} - \tau A^{q/(1+q)} = - \int_0^t dt' A(t'). \tag{40}$$

Since $\tau = p \int_0^t dt' A^{1/(1+q)}(t')$ can be expressed through $A(t)$, we conclude that equation (40) is a closed equation for $A(t)$. It appears impossible, however, to find an explicit solution for $A(t)$ or for $A(\tau)$. Therefore, we proceed to determine $\tau(A)$. Differentiating equation (40) with respect to A yields

$$\frac{q}{1+q} (A^{-1} - \tau A^{-1/(1+q)}) + \frac{q}{p} A^{q/(1+q)} \frac{d\tau}{dA} = 0. \tag{41}$$

In deriving equation (41), we have applied the chain rule $\frac{d}{dA} = \frac{d\tau}{dA} \frac{dt}{d\tau} \frac{d}{dt}$, and $\tau = p \int_0^t dt' A^{1/(1+q)}(t')$ to evaluate the derivative of the right-hand side of equation (40).

We now multiply equation (41) by $A^{-1/(1+q)}$ and then integrate to find an explicit expression for $\tau(A)$

$$\tau = p [A^{-q/(1+q)} - A^{p/(1+q)}]. \tag{42}$$

One can verify that this expression is consistent with the expected short-time behaviours $A \simeq 1 - (1+q)t$ and $\tau \simeq pt$ implied by equations (35) and (36). In the long-time limit, the above expression yields the leading asymptotic behaviour of the density and the mass

$$A(t) \simeq \frac{q}{1+q} t^{-1} \quad M(t) \simeq \frac{1}{1+q} t^{-1}. \tag{43}$$

Hence, these densities decay with the same universal exponent as in the product-kernel model. Again, the average active mass remains finite $\langle k \rangle = M/A \rightarrow 1/q$ for $t \rightarrow \infty$. One slight difference from the product kernel is that the average mass diverges in the limit $q \rightarrow 0$.

To determine \mathcal{A}_k , we again employ the Lagrange inversion formula. From the exponentiated form of equation (38), $\mathcal{A} e^{-\tau \mathcal{A}} = e^z$, we immediately find $\mathcal{A}_k = (k\tau)^{k-1}/k!$, or $A_k(t) = (k\tau)^{k-1} \exp\{- \int_0^t dt' [kA(t') + M(t')]\}/k!$. Using equations (40) and (42), the mass distribution of active clusters is obtained in terms of the variable $v = A^{1/(1+q)}$

$$A_k(v) = v^{1+q} \frac{[kp(1-v)]^{k-1}}{k!} e^{-kp(1-v)}. \tag{44}$$

Although the variable v is quite different, the similarity with the corresponding product-kernel expression (28) is striking. The monomer density in this case is $A_1 = A \exp[-p(1 - A^{1/(1+q)})]$. Therefore, it follows the same t^{-1} asymptotic decay as in the product-kernel case.

The appropriate large-mass and large-time limit is again taken in such a way, that the scaling variable $\xi = kqv$ is kept finite. The corresponding characteristic size grows according to $k^* \sim t^{1/(1+q)}$. The mass distribution of active clusters can again be recast into the following scaling-like form:

$$A_k(t) \sim e^{-\Lambda(q)k} k^{-3/2} t^{-1} F(\xi) \quad (45)$$

with $\Lambda(q) = -q - \ln(1 - q)$, and with the scaling function $F(\xi) = e^{-\xi}$. The numerous similarities between corresponding expressions in the product- and sum-kernel solutions reflect the similar underlying mathematical structure of both models. For example, the distributions generally decay exponentially. Furthermore, in the limit $q \rightarrow 0$, there is an intermediate regime $k \ll q^{-2}$, where an algebraic decay $A_k(t) \sim k^{-3/2}$ occurs.

We analysed the mass distribution of passive clusters in a similar way as for the product-kernel model. For example, the final distribution is given by

$$P_k(\infty) = \frac{q}{p} \int_0^1 dx x^q [(kj + 1) + kpx] \frac{[kp(1-x)]^{k-1}}{k!} e^{-kp(1-x)} \quad (46)$$

which may be rewritten explicitly through the beta function and the confluent hypergeometric function. Interestingly, the leading large-mass behaviour of the final distribution is *identical* to that obtained for the product-kernel case (33). Additionally, the time-dependent behaviour can be rewritten using the form (34) with the argument of the Gamma function now being $1 + q$ (instead of q).

6. Discussion

We have analysed a class of stochastic-aggregation processes. We have solved for the three classical reaction kernels: $1, i + j$ and ij . Our methods are also applicable to the linear combination $K(i, j) = a + b(i + j) + cij$, with a, b and c non-negative constants [13, 14], and to the reaction kernel $K(i, j) = 2 - r^i - r^j$, where $0 < r < 1$ [15].

We have observed that stochastic aggregation exhibits a variety of universal features. For instance, the final number density of passive clusters is identical in all three models. Also, the number density of active clusters decays as t^{-1} . The former feature has been explained by a simple argument; remarkably, it remains valid even beyond the scope of the rate equations. It would be interesting to understand the latter feature within a coherent model-independent framework. For the constant and sum kernels, we have seen that the number density, the monomer density and the mass density all decay according to t^{-1} . Furthermore, the results suggest that the following scaling-like form:

$$A_k(t) \simeq \rho_k t^{-1} F(\xi) \quad (47)$$

applies when the kernel grows indefinitely with the mass. For the solvable sum and product kernels, ρ_k decays exponentially in the large-mass limit. It will be interesting to study whether this exponential behaviour applies for more general kernels, e.g., for homogeneous kernels, $K(ai, aj) = a^\lambda K(i, j)$, with a positive homogeneity index $\lambda > 0$.

The simplest constant-kernel model is special, and it exhibits the most interesting behaviour. We have shown that in this case the final mass distribution of passive clusters is algebraic. The decay exponent is governed by the probability p , and the entire range of decay exponents, consistent with mass conservation is possible. The time-dependent behaviour

follows ordinary scaling, and the corresponding mass scale grows algebraically with a non-universal (p -dependent) exponent.

Very similar behaviours were found for the product and sum kernels. In general, the mass distributions decay exponentially, and the average mass approaches a finite value. In the limit $q \rightarrow 0$, corresponding to the original aggregation process, an algebraic mass decay occurs in the intermediate mass range $k \ll q^{-2}$. The time-dependent behaviour does not follow ordinary scaling, as the distributions are dominated by time-independent exponential factors. Nevertheless, a corrective factor which is governed by an algebraically growing scale was found to be relevant. Remarkably, although the models exhibit different temporal behaviours, they possess the same large-mass behaviour of the final mass distribution.

The above stochastic aggregation provides an interpolation between aggregation ($p = 1$) and annihilation ($p = 0$) processes. Therefore, it may be used as a tool for studying either problem. For example, the Smoluchowski aggregation equations may be applied to low-dimensional processes using effective reaction rates. Hence, the above solution of the master equations may be relevant to reaction-diffusion problems.

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